Transition-metal Carbonyl Derivatives of the Germanes. Part 9.[1] Reactions of Tetracarbonyldi(methylgermyl)iron with Some Covalent Halides

By **Alan Bonny** and **Kenneth M. Mackay**,* School of Science, University of Waikato, Hamilton, New Zealand

The reactivity patterns of [Fe(CO)$_4$(GeMeH$_2$)$_2$] (1), with covalent halides have been established from ^{1}H n.m.r., i.r., and mass-spectral studies. Halogenation by milder reagents such as SiCl$_4$ is stepwise and alternate at each germanium. The more reactive hydrogen halides substitute and then cleave Fe–Ge bonds. The germyliron system is intermediate in its tendency to cleavage between the germyl-manganese and the -cobalt carbonyls. Rearrangement to cyclic compounds [{Fe(CO)$_4$(GeMeCl$_x$H$_{1-x}$)}$_2$] is observed after longer reaction times.

EARLIER studies [2] of [Mn(CO)$_5$(GeH$_3$)] and of the methylgermyl [3] or rhenium [4] analogues showed that many covalent halides reacted with these compounds to give stepwise replacement of the H atoms. Group 4 tetrachlorides, hydrogen halides, mercury(II) halides, and PCl$_3$ all so reacted to different extents: thus SnCl$_4$ was more reactive than GeCl$_4$ or CCl$_4$ while SiCl$_4$ did not react at all. Cleavage of the Mn–Ge bond was observed [3] only for much more vigorous reagents, even bromine giving more substitution than cleavage with [Mn(CO)$_5$(GeMeH$_2$)]. In contrast, cleavage of the bond to cobalt was the principal reaction reported for such reagents with germyl- [5] or silyl-tetracarbonylcobalt.[6] For example, the cleavage reaction of the cobalt compounds with mercury(II) halides is quantitative and useful for analysis.

Hydrogen-1 n.m.r. data (τ) [a]

Compound	CH$_3$ (triplet)	GeH$_2$ (quartet)	^3J/Hz	CH$_3$ (doublet)	GeH (quartet)	^3J/Hz	CH$_3$ (singlet)	Notes
(1)	9.30	6.20	3.8					b
(2)	9.26	6.24	3.8	8.84	4.32	2.8		b
(3)				8.75	4.32	2.7		b
(4)				8.75	4.13	2.6	8.50	b
(5)							8.38	c
(6)				9.10	4.12	3.0		c, d
(7)				8.96	4.23	2.8	8.80	c
(8)							8.44	c, e

[a] Derived from clear signals in the different reactions and are averaged. Different individual values agreed within τ 0.06 and 0.2 Hz. Relative intensities are consistent with assignments. [b] Values from SiCl$_4$, CS$_2$, or CCl$_4$ solutions. [c] Value from benzene solution (HCl reaction). [d] Compound (6) also shows a signal at τ 20.48. [e] Also observed in CHCl$_3$ at τ 8.52.

It was thus of interest to examine the germyl–iron carbonyl system, both to compare with the manganese and cobalt species and to observe the substitution pattern when two germyl groups are present. The study was made using ^{1}H n.m.r. to follow the reactions of [Fe(CO)$_4$(GeMeH$_2$)$_2$] (1) with CCl$_4$, SiCl$_4$, SnCl$_4$, HCl, HgCl$_2$, and related halides. Since (1) condenses slowly [7] to [{Fe(CO)$_4$(GeMeH)}$_2$], and the dimethylgermyl analogue condenses very rapidly [8] to [{Fe(CO)$_4$(GeMe$_2$)}$_2$], the formation of chloride derivatives of [{Fe(CO)$_4$(GeMeH)}$_2$] is an additional possibility.

EXPERIMENTAL

Manipulations and spectroscopic measurements were made as described [3,7] previously. Solvents were purified and rigorously dried before use. The head fraction was pumped off from the covalent halides to ensure removal of all traces of hydrogen halide. Tetracarbonyldi(methylgermyl)iron, (1), was prepared [7] by alkali-metal halide elimination. Mass spectra of mixtures of solid products were run at different probe temperatures, *e.g.* 25 and 50 °C, to use the differences in intensities arising from different volatilities as an aid to assigning fragment ions.

General Method.—A sample of (1), with SiMe$_4$ and solvent where necessary, was condensed with the reactant into an n.m.r. tube. This was sealed and the reaction was monitored by following the changing resonances. In the various systems studied, n.m.r. signals were found suggesting a range of new compounds (2)—(8). Their ^{1}H n.m.r. parameters are collected in the Table and their identification is discussed in the Results section. Compounds (2)—(5) are respectively mono-, di-, tri-, and tetra-chloro-derivatives of (1), (6) is [Fe(CO)$_4$(GeMeClH)H], while (7) and (8) are chloro-substituted condensed species. The reactions of (1) were very much faster than those of the manganese [3] species, and the clearest sequence of changes was found with the relatively unreactive SiCl$_4$. This system is detailed first as an example.

(*i*) (1) + SiCl$_4$.—(*a*) About 0.06 mmol of (1) dissolved in SiCl$_4$ (0.3 cm^3) showed no reaction at −20 °C. After 8 h at 25 °C the methyl doublet of the first product, (2),

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[2] R. D. George, K. M. Mackay, and S. R. Stobart, *J.C.S. Dalton*, 1972, 1505.

[3] B. W. L. Graham, K. M. Mackay, and S. R. Stobart, *J.C.S. Dalton*, 1975, 475.

[4] K. M. Mackay and S. R. Stobart, *J.C.S. Dalton*, 1973, 214.

[5] R. D. George, K. M. Mackay, and S. R. Stobart, *J.C.S. Dalton*, 1972, 974.

[6] B. J. Aylett and J. M. Campbell, *J. Chem. Soc.* (*A*), 1969, 1910.

[7] Part 6, A. Bonny and K. M. Mackay, *J.C.S. Dalton*, 1978, 506.

[8] Part 7, A. Bonny and K. M. Mackay, *J.C.S. Dalton*, 1978, 722.

appeared at τ 8.88. Continued reaction produced a second product, (3), and ultimately a third, (4), with proportions after 40 h of 48 (1), 33 (2), and 9% (3), and after 80 h of 34 : 55 : 11. The consumption of (1) almost ceased after 120 h, the proportion of (2) passed through a maximum at 100 h, (4) appeared after 20 d, and a white solid precipitated. After 1 month, species remaining in solution accounted for about two thirds of the initial signal intensity, in the proportions 29 (1), 50 (2), 9 (3), and 11% (4).

(*b*) 0.16 mmol of (1) reacted in CS_2 solution with $SiCl_4$ (0.59 mmol) in a similar manner except that a further species X [τ 8.88 (d) and 4.68 (q), *J* 2.0 Hz] was found. After 40 and 80 h at 25 °C the proportions were 84 (1), 12 (2), 4% X, and 52 (1), 25 (2), 2 (3), 2 (4), and 18% (X) respectively.

In both (*a*) and (*b*), singlets attributed to chlorosilanes [9] were seen at τ 3.4, 4.7, and 5.4.

(*ii*) (1) + CCl_4.—A 5% solution of (1) in CCl_4 reacted rapidly as soon as it started to melt and a white solid deposited. A fast initial scan showed a poorly resolved doublet (τ 8.8, *J* 3 Hz) attributable to (2) or (3) and a singlet due to $CHCl_3$ at τ 2.73. After 10 min, 95% of the signal intensity was a singlet at τ 8.22 plus $CHCl_3$. The white precipitate contained 26.16% Cl.

(*iii*) (1) + $HgCl_2$.—A 10% solution of (1) in $SiCl_4$ reacted rapidly with an excess of $HgCl_2$. After 3 h at 0 °C the composition was 74 (1), 7 (2), 10 (3), and 5% (4) together with $GeMeClH_2$. After another 2 h at room temperature the rapid reaction was complete, a singlet attributed to a further product (5) was found giving 40 (1), 15 (2), 20 (3), 10 (4), and 5% (5) with 10% $GeMeClH_2$. A much slower reaction with the $SiCl_4$ ensued and a spectrum run after 3 months at 0 °C showed almost complete reaction of (1) and (2), allowing the weak GeH quartets of (3) and (4) to be more certainly assigned. The signal strenths of (4) and (5) were unchanged and the proportion of (3) had increased to 65%.

(*iv*) (1) + HCl.—The reaction of (1) (38 mg, 0.11 mmol) and HCl (0.27 mmol) was fast in benzene at 5 °C. Signals indicated the formation of (2), a new species (6) (Table), $GeMeClH_2$ (τ 9.78 and 5.05, *J* 3.0 Hz), $GeMeCl_2H$ (τ 9.60 and 3.91, *J* 1.3 Hz), $GeMeCl_3$ (τ 8.61), $[Fe(CO)_4H_2]$ (τ 19.98), together with an unidentified doublet (τ 9.08, *J* 2.8 Hz), some weak singlets, and H_2. The relative proportions after various periods at 5 °C were:

t/min	(1)	(2)	(6)	$GeMeClH_2$	Singlet (τ 8.77)	Doublet (τ 9.08)
7	64	12	11	*ca.* 12	1	
25	32	*ca.* 8	31	29	1	
120	11	*ca.* 7	39	41	1	1
540			38	39	9	1

The last sample also showed $GeMeCl_2H$ (14%) and $[Fe(CO)_4H_2]$ (1%). The HCl was consumed within 2 h at 5 °C and H_2 was found [10] in all the samples.

After 10 d at 25 °C a yellow precipitate was present and signals were found from (5) (9%), (6) (4%), a further new species (7) (9%), $GeMeClH_2$ (20%), $GeMeCl_2H$ (23%), $GeMeCl_3$ (4%), $[Fe(CO)_4H_2]$ (1%), τ 9.08 (d) (4%), τ 8.77 (s) (18%), and τ 8.52 (s) [perhaps (8)] (8%).

After 12 months there remained only the resonances of $GeMeCl_2H$, $GeMeCl_3$ (both strong), (5), (7) (both medium-weak), (8) (very weak), and two weak unidentified singlets, and yellow tabular crystals had formed. Volatiles were removed yielding *ca.* 350 μmols of incondensable gas [very weak ν(CO), assumed to be a mixture of H_2 and CO]. Yellow crystals were hand separated from a yellow amorphous solid and identified * by mass, i.r., and ^1H n.m.r. spectra as the new compound, (8) (see Table). The mass and i.r. spectra of the amorphous solid indicated a mixture of (5) and (8) together with higher-molecular-weight species. The i.r. spectrum showed the following new absorptions besides those due to (8): 2 078m,br (sh), 2 076.5w (sh), 2 068mw, 2 057.2w (sh), *ca.* 2 054w (sh), 2 051s, 2 049vs, 2 031.5mw, 2 021.7mw, 2 016.3w, 2 006.6m, 1 995w,br [all ν(CO)]; *ca.* 800vw, 785w [$\rho(CH_3)$]; 672vw, 614m (sh), 608ms [δ(FeCO)]; and *ca.* 590vw (sh) cm^{-1} [ν(GeC)]. In the mass spectrum of the amorphous solid, in addition to envelopes attributed to compounds (5) and (8), a series of envelopes at *m*/*e* 590—598, 564—572, 536—544, 508—518, and 480—488 could be attributed to ions such as $[Fe_3(CO)_n(GeMeCl_2)_2]^+$ (n = 4—0).

(*v*) (1) + $SnCl_4$.—Compound (1) (0.06 mmol) and $SnCl_4$ (0.05 mmol) were allowed to react in n-hexane (0.3 cm^3) [11] for 7.5 h at −95 to −72 °C with continuous removal of the HCl and chloro(methyl)germanes formed. The n.m.r. spectrum was poor, because of suspended solids, but indicated (1), (2), and (3) in the ratio *ca.* 3 : 60 : 40. After further handling the relative proportions of (2) and (3) had reversed to 40 : 60.

Volatiles were removed giving a pale yellow solid which turned orange in 15 min in the dark at room temperature. Mass spectra of the solid recorded at five different probe temperatures up to 100 °C allowed the identification of the fragment-ion families of (2), (7), and (8), besides those [7] of (1) and $[\{Fe(CO)_4(GeMeH)\}_2]$. At a probe temperature of 110 °C a series of irregularly space envelopes with polyiron (but no Ge nor Cl) shapes were observed up to *m*/*e* 629.

The i.r. spectrum of the residues showed very weak absorptions attributable [7] to (1) and $[\{Fe(CO)_4(GeMeH)\}_2]$, four ν(CO) bands assigned to (8) [2 076.5vw (sh), 2 083.6s, 2 029w (sh), and 2 027vvs cm^{-1}], together with bands at 2 137vw,br, 2 122vw,br, 2 109.2vs*, 2 093.6s, *ca.* 2 088vw (sh), 2 079.2w (sh), 2 067.8vs, 2 063w (sh), *ca.* 2 058w*, 2 051.8s,br*, *ca.* 2 044vw (sh), 2 040.5mw*, 2 037mw*, *ca.* 2 033.5w,br (sh), 2 019.5s (sh), 2 016w, 2 012.7s (sh) [all ν(CO) with ν(GeH) possibly contributing to the 2 037—2 058 absorptions); 856mw, 800m,br, 708m,vbr [$\rho(CH_3)$ and δ(GeH)]; 650mw,vbr [δ(GeH)]; 617m, 611vvs [δ(FeCO)]; 590mw (sh) [ν(GeC)]; *ca.* 540w,vbr [δ(FeCO)]; 470w,br, 430w,br [ν(FeC)]; and 374mw,br cm^{-1} [ν(GeCl)]. Absorptions marked with an asterisk were observed to decrease in relative intensity with time and may thus be attributable to (2) and (3).

Brief studies were made of three further reactions.

(*vi*) (1) + $SiBr_4$.—A *ca.* 5% solution of (1) in $SiBr_4$ solvent was observed to react at room temperature with *ca.* 10% conversion into a new GeMeH(X)Y species in 2 h. By analogy with the slower $SiCl_4$ reaction, this is probably $[Fe(CO)_4(GeBrMeH)(GeMeH_2)]$. A few brown crystals had

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* Mass-spectral data for compounds (2), (3), (5), (7), and (8) and the i.r. spectrum of (8) are available as Supplementary Publication No. SUP 72320 (4 pp.). For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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deposited in the tube after 1 year and these were identified by mass spectrometry as $[\{Fe(CO)_4(GeBrMe)\}_2]$. Principal fragment ions were $[\{Fe(GeBrMe)\}_2(CO)_n]^+$ ($n = 0$—8) [a relatively weak parent ion as found for (7) and (8), and for the complexes $[\{Fe(CO)_4(GeMeR)\}_2]$ (R = H [7] or Me [8])] and $[FeGe_2Me_x]^+$ ($x = 0$—2).

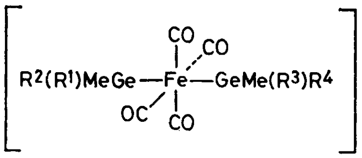
(*vii*) (1) + HBr.—Hydrogen-1 n.m.r. spectral data indicate a similar route to the HCl reaction but the reaction was faster. Thus signals attributable to $[Fe(CO)_4(GeBrMeH)H]$ and $GeBrMeH_2$ were the major initial products. Further GeMeH-containing species, and a second high-field signal due to $[Fe(CO)_4H_2]$, appeared later in the reaction.

(*viii*) (1) + PCl_3.—A 10% solution of (1) in PCl_3 showed no ^1H n.m.r. evidence for reaction after 21 h at ambient temperatures. After 1 year the tube contained a dark brown liquid and solids. The volatile fraction consisted of CO, H_2, $GeMeCl\text{-}H_{3-x}$ ($x = 1$—3), and PCl_3. The mass spectrum of the involatile residues indicated only polychlorophosphorus-containing ions.

RESULTS

Spectroscopic Identification.—Although most of the compounds were available only in mixtures, reasonably probable identifications were possible from the observed spectra.

The ^1H n.m.r. data collected in the Table are consistent with the species (2)—(5) being the stepwise chlorination products of (1), with substitution on alternate germanium atoms. Replacement of H by Cl causes a downfield shift of *ca.* 0.4 p.p.m. in the Me resonance, and one of *ca.* 2 p.p.m. in the GeH resonance. Further, ^3J decreased by *ca.* 1 Hz. These changes closely parallel those observed [3] for chlorine substitution in methylgermanes and in $[Mn(CO)_5(GeMeH_2)]$. In the monochloride (2) there is a small but definite upfield shift of the GeH_2 resonance in the unsubstituted $GeMeH_2$ group compared with (1). This is the result of the anisotropic diamagnetism induced in the GeCl bond and is consistent with (2) retaining the *cis* configuration of (1).



(1) $R^1 = R^2 = R^3 = R^4 = H$

(2) $R = R^2 = R^3 = H$; $R^4 = Cl$

(3) $R^1 = R^3 = H$; $R^2 = R^4 = Cl$

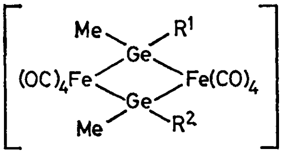
(4) $R^1 = H$; $R^2 = R^3 = R^4 = Cl$

(5) $R^1 = R^2 = R^3 = R^4 = Cl$

Compound (6) shows a high-field resonance close to that of $[Fe(CO)_4H_2]$ together with the shifts of a monosubstituted germyl group and is thus formulated as $[Fe(CO)_4(GeMeClH)H]$.

Compounds (7) and (8) are formulated as derivatives of the cyclic condensation product $[Fe_2(CO)_8(GeMeH)_2]$ known [8] to be derived from (1).

The slightest n.m.r. evidence, lone singlets, is that adduced for the fully chlorinated species (5) and (8). Fortunately, it is these two compounds for which the mass-spectral evidence is strongest. The HCl reaction mixture, which had been allowed to stand for 1 year, gave (8) as a crystalline product and (5) as a major component of the residue. The major ions of the tetrachloride (5) are listed in SUP 22320. Although the parent ion was not observed, $[P - Cl]^+$ was relatively strong and $[P - Me]^+$ was also found. This compares with other $[Fe(CO)_4(GeR_3)_2]$ species where the parent ion was weak for $R_3 = GeMeH_2$,[7] H_3,[12] and Cl_3,[13] while $[Ru(CO)_4(GeCl_3)_2]$ showed [14] no parent ion but had $[P - Cl]^+$ as the ion of highest mass. Compared with (1), the ions of (5) which arise from Fe–Ge fission are more prominent. The only metastable ion found corresponds to CO loss from the base-peak ion $[Fe(CO)Ge_2Me_2Cl_4]^+$. The widely observed stepwise carbonyl loss occurs for (5) with $[P - 2CO]^+$ mw, $[P - 3CO]^+$ vs, and $[P - 4CO]^+$ s, but $[P - CO]^+$ was not observed although, in parallel with the parent, $[P - CO - Cl]^+$ was evident.



Condensation product $R^1 = R^2 = H$

(7) $R^1 = H$, $R^2 = Cl$

(8) $R^1 = R^2 = Cl$

For compound (8) both the mass and i.r. spectra support the formulation as $[\{Fe(CO)_4(GeMeCl)\}_2]$. In the mass spectrum the parent ion was very weak and all the carbonyl-loss ions $[P - nCO]^+$ were found with intensities decreasing in the order $n = 7 > 6{,}8 > 1{,}4 > 5 > 3 > 2 > 0$, a pattern similar to those found for [7] $[\{Fe(CO)_4(GeMe_2)\}_2]$ and for [8] $[\{Fe(CO)_4(GeMeH)\}_2]$. The $[FeGe_2Me_2]^+$ and $[FeGe_2CH_x]^+$ ions were also intense while Cl or Me loss from the $[P - nCO]^+$ ions was a minor process. Metastable ions confirmed the CO loss steps for $n = 1$—6.

The i.r. spectrum was also very similar to those [7,8] of related compounds. At lower frequencies a methyl rock was evident at 762 cm^{-1} and carbonyl-bending modes were found near 610 cm^{-1}. In the carbonyl-stretching region the three prominent fundamentals at 2 074, 2 028, and 2 013 cm^{-1} show the expected shift to higher frequency compared with $[\{Fe(CO)_4(GeMe_2)\}_2]$ or $[\{Fe(CO)_4(GeMeH)\}_2]$. The C_{2h} isomer would show only the out-of-phase modes in the i.r. while for the C_{2v} isomer these, although allowed, are probably weak. Since the ^1H n.m.r. spectrum shows only one signal no clear conclusion about isomeric composition may be drawn. Either the major component is C_{2v}, accounting for all the absorptions, or the main component is C_{2h} with a minor proportion of the C_{2v} isomer accounting for the weak modes. The 2 028 cm^{-1} contour is clearly asymmetric and both the b_u (a_1 and b_1) modes are assigned to it. The analogous frequencies were just separated in the spectrum of $[\{Fe(CO)_4(GeMeH)\}_2]$.

The remaining species were not obtained pure or as dominant components, but it was possible to pick out the main families of ions arising from (2), (3), and (7) from mass spectra, especially of the $SnCl_4$ reaction. These all show weak parent ions and stepwise loss of CO. For both (2) and (3), hydrogen or CH_x loss was only minor from ions

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[14] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 2874.

retaining CO and there is no loss of single H atoms; thus for the ion $[\mathrm{Fe(CO)_2Ge_2Me_2Cl_2H^1}]^+$ from (3) the ratios for $x = 2 : 1 : 0 = 6 : 0 : 1$.

The Reactions.—Tetrachlorosilane reacts slowly with $[\mathrm{Fe(CO)_4(GeMeH_2)_2}]$ according to equation (1) leaving

$$(1) + \mathrm{SiCl_4} \longrightarrow \underset{(2)}{[\mathrm{Fe(CO)_4(GeMeClH)(GeMeH_2)}]} + \underset{(3)}{[\mathrm{Fe(CO)_4(GeMeClH)_2}]} + \underset{(4)}{[\mathrm{Fe(CO)_4(GeMeCl_2)(GeMeClH)}]} \qquad (1)$$

unchanged starting material despite a 10-fold excess of $\mathrm{SiCl_4}$. In $\mathrm{CS_2}$ solution the reaction was similar but slower and forming an additional product X whose n.m.r. suggests it contains the GeMeClH group. X may arise from interaction with the solvent.

Carbon tetrachloride reacts very rapidly with (1) with more complete substitution. The reaction of $\mathrm{HgCl_2}$ followed a similar path but with *ca.* 10% of the germanium

$$(1) + \mathrm{CCl_4} \longrightarrow (2) \longrightarrow (3) \longrightarrow (4) + \underset{(5)}{[\mathrm{Fe(CO)_4(GeMeCl_2)_2}]} \qquad (2)$$

$$(1) + \mathrm{HgCl_2} \longrightarrow (2) + (3) + (4) + (5) + \mathrm{GeMeClH_2} \qquad (3)$$

in the cleavage product, $\mathrm{GeMeClH_2}$. All the four halogeno-derivatives were formed. At least part of the mercury was reduced to the metal.

The reaction of HCl was fast and more complex. Initially (2) is formed but one group is then cleaved. Equal

$$(1) + \mathrm{HCl} \longrightarrow (2) + \mathrm{H_2} \qquad (4a)$$

$$(2) + \mathrm{HCl} \longrightarrow \underset{(6)}{[\mathrm{Fe(CO)_4(GeMeClH)H}]} + \mathrm{GeMeClH_2} \qquad (4b)$$

quantities of (6) and $\mathrm{GeMeCl_2H}$ form during this stage of the reaction, and these are the major components at the point where the HCl is consumed. In the next stage, the residual (1) and (2) are consumed, $\mathrm{GeMeClH_2}$ and (6) remain the major components, $\mathrm{GeMeCl_2H}$ and a small amount of $[\mathrm{Fe(CO)_4H_2}]$ appear, but a detailed interpretation is impossible since *ca.* 10% of the methyl groups are in unidentified species. A second cleavage analogous to (4b) can only be a minor process. Ten days later the cyclic species (7) and perhaps (8) had appeared together with (5) and the chloro(methyl)germanes. Thus (5) was not formed by halogenation of (1) or (2) nor were (7) and (8) formed by condensation of halide derivatives of (1) but these species must arise directly or indirectly from (6). After 1 year the main iron–germanium species remaining in solution were (5) and (7), while the solids contained mainly (5), (8), and higher-molecular-weight species. The i.r., with 12 carbonyl modes, and mass spectra indicate the latter is of at least the complexity of $[\mathrm{Fe_3(CO)_{12}(Ge_2Me_2Cl_4)}]$.

Since $\mathrm{SnCl_4}$ is known [15] to react with hydrides the re-

$$\mathrm{SnCl_4} + \mathrm{Ge{-}H} \longrightarrow \mathrm{Ge{-}Cl} + \mathrm{SnCl_2} + \mathrm{HCl} \qquad (5)$$

action between (1) and $\mathrm{SnCl_4}$ was carried out with continuous removal of HCl. The reaction proceeded extensively at −72 °C, yielding both the mono- and di-chlorides, (2) and (3), although less than a 1 : 1 mol ratio of $\mathrm{SnCl_4}$ was used. From the proportions of (1) and (2) and the small amount of unchanged (1) it appears that *ca.* 1.5 Cl per $\mathrm{SnCl_4}$ had reacted, suggesting that about half the HCl of equation (5) had reacted *via* (4a). The absence of (6) shows there was no further reaction of HCl. The common result [3,15,16] of reaction of hydride with a deficit of $\mathrm{SnCl_4}$ is to form almost entirely the monochloride, while this reaction of (1) is closer to that [16] of $\mathrm{N(SiH_3)_3}$ in showing monosubstitution on more than one equivalent $\mathrm{MH_3}$ group. However, uncertainties arise over the degree of participation of HCl.

In this system, samples which had been removed from the n.m.r. tube for further spectroscopic investigation showed substantial amounts of the cyclic condensation product $[\{\mathrm{Fe(CO)_4(GeMeH)}\}_2]$ and its chlorides (7) and (8). Since colour changes were observed even in the sealed tube, in contrast to the $\mathrm{SiCl_4}$ or $\mathrm{CCl_4}$ reactions, $\mathrm{SnCl_2}$ is a likely catalyst and the changes may also be assisted by trace amounts of oxygen in the nitrogen or argon atmospheres. As only a small amount of changed (1) remained, and as (2) was consumed in preference to (3), it is probable that $[\{\mathrm{Fe(CO)_4(GeMeH)}\}_2]$ and its monochloride, (7), were formed by elimination from (2) of $\mathrm{GeMeClH_2}$ or $\mathrm{GeMeH_3}$ respectively. Similarly, (8) could arise either from (2) or (3). Formation of $[\{\mathrm{Fe(CO)_4(GeMeH)}\}_2]$ and subsequent chlorination to (7) and (8) seems less likely since the active chlorinating agents had been consumed at this stage.

The initial studies suggest that the reactions of $\mathrm{SiBr_4}$ and of HBr parallel those of the chlorides but are faster. The formation of the bromine analogues of (2), (6), and (8) was indicated. Phosphorus trichloride reacted very slowly and no germyliron products were identified.

DISCUSSION

The reactions of $[\mathrm{Fe(CO)_4(GeMeH_2)_2}]$ are much closer to those [3] of $[\mathrm{Mn(CO)_5(GeMeH_2)}]$ than to those [5] of the germylcobalt compounds. Stepwise substitution of halogen for hydrogen is the dominant reaction of the relatively unreactive covalent halides and this occurs on alternate germanium atoms. However, the $\mathrm{HgCl_2}$ system showed a minor route involving Fe–Ge cleavage and the reaction of HCl was cleavage following an initial substitution. Thus the tendency for M–Ge cleavage to dominate over Ge–H cleavage in the germylmetal carbonyls lies in the sequence $\mathrm{Co} > \mathrm{Fe} > \mathrm{Mn}$. The rates of reaction of the Ge–H bonds are much higher for the iron compounds than for the manganese ones illustrated for example by the speed of the $\mathrm{CCl_4}$ reaction, by the low temperature of the $\mathrm{SnCl_4}$ reaction, and by the reactivity of $\mathrm{SiCl_4}$.

The condensation [7] of (1) to $[\{\mathrm{Fe(CO)_4(GeMeH)}\}_2]$ is slow on its own in the dark and more rapid in light or in the presence of reaction residues. While there is good evidence for (8) and clear indications of the monochloride, (7), these did not seem to be formed readily, if at all, by (2)—(4), the chloro-derivatives of (1). Compounds (7) and (8) were formed in the HCl system but from the hydride (6), and not from (1) or (2) which were

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[15] F. S. Wong, M.Sc. Thesis, University of Waikāto, 1976; J. E. Bentham, S. Cradock, and E. A. V. Ebsworth, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1107; N. S. Hosmane, *ibid.*, 1974, **10**, 1077.

[16] S. Cradock, E. A. V. Ebsworth, and N. Hosmane, *J.C.S. Dalton*, 1975, 1624.

consumed in the earlier stages. The formation of (7) and (8) from a mixture containing (1)—(3) did occur in the $SnCl_4$ reaction but not from similar mixtures in the $SiCl_4$ or $HgCl_2$ studies, suggesting catalysis of the cyclisation by $SnCl_2$ or other residues. The cyclic bromide $[\{Fe(CO)_4(GeBrMe)\}_2]$ did occur in the $SiBr_4$ reaction, but only after standing for a long time.

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